

Crystal structures of diphosphinated group 6 Fischer alkoxy carbenes

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The crystal structures of four diphosphinated Group 6 Fischer alkoxy carbenes with the compositions *fac*-(dppe)(CO)₃M=C(OR')(R) (R = Me, R' = Et, M = Cr, **1**; R = Ph, R' = Me, M = Cr, **2**; R = Me, R' = Me, M = W, **3**; R/OR' = 3-methyl-2-oxacyclopentylidenyl, M = Cr, **4**) have been determined at 243 K. Compound **1** crystallizes in the monoclinic system, space group *P*2₁/*c* with *a* = 11.2243(11) Å, *b* = 18.5998(18) Å, *c* = 15.1260(15) Å, β = 107.056(4)°, *V* = 3019.0(5) Å³, and *Z* = 4. Compound **2** crystallizes in the monoclinic system, space group *P*2₁/*c* with *a* = 11.8102(9) Å, *b* = 18.3152(14) Å, *c* = 15.0262(12) Å, β = 93.753(3)°, *V* = 3243.3(4) Å³, and *Z* = 4. Compound **3** crystallizes in the monoclinic system, space group *P*2₁/*c* with *a* = 11.3458(6) Å, *b* = 18.5772(9) Å, *c* = 15.3883(8) Å, β = 108.576(6)°, *V* = 3074.5(3) Å³, and *Z* = 4. Compound **4** crystallizes in the orthorhombic system, space group *Pna*2₁ with *a* = 22.6509(14) Å, *b* = 9.8118(6) Å, *c* = 13.7507(8) Å, *V* = 3056.0(3) Å³, and *Z* = 4. Steric repulsions with the dppe ligand favor a conformation with the alkoxy moiety directed toward the dppe backbone, in an *E* geometry, in **1–4**.

KEY WORDS: Fischer carbenes; diphosphine; X-ray structure; 2-oxacyclopentylidene; dppe; conformation.

Introduction

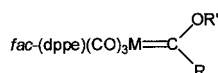
The first report of the preparation and X-ray structure analysis of a monophosphinated Fischer alkoxy carbene was in 1966.¹ Monophosphination of Group 6 Fischer alkoxy carbenes has since been reported to confer additional reactivity, upon deprotonation, in reaction with electrophiles,² to alter product distributions in cycloaddition reactions including the Dötz reaction,³ and in one example using a chiral phosphine, to induce asymmet-

ric synthesis in the preparation of cyclopropanes.⁴ Neutral, diphosphinated Group 6 Fischer alkoxy carbenes have only been reported much more recently but with no supporting X-ray structure analyses included.^{5,6} Herein, we describe the single crystal X-ray structures of four diphosphinated Group 6 Fischer alkoxy carbenes containing a chelating 1,2-bis(diphenylphosphino)ethane (dppe) ligand, including three previously unreported compounds (**2–4**), whose compositions are indicated in Scheme 1.

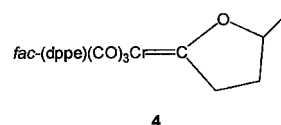
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1 R = Me, R' = Et, M = Cr
2 R = Ph, R' = Me, M = Cr
3 R = Me, R' = Me, M = W



4

Experimental

Preparations

Compounds **1** and **2** were prepared by thermal substitution of the corresponding pentacarbonyl alkoxy carbene by dppe according to the following general procedure, using standard Schlenk techniques:⁽³⁾⁷⁽⁴⁾ An equimolar amount of the requisite pentacarbonyl alkoxy carbene⁽⁵⁾⁸ and dppe were dissolved in a 3:1 mixture of hexanes/benzene followed by heating the stirred mixture, under nitrogen, to reflux for 4 h. After cooling to room temperature, the red to red-orange precipitates were collected by filtration, washed with hexanes, and dried in vacuo. The products were obtained in 60–80% yield.

Compound **3** was made using the same procedure as **1** and **2**, except that toluene solvent was used in place of a 3:1 mixture of hexanes/benzene.⁽⁵⁾⁸ The crude product which contains a mixture of *fac* and *mer* isomers was eluted on a flash column using 85:15 petroleum ether/diethyl ether, giving the *fac* isomer as the minor product in the second red band.

Compound **4** was prepared from deprotonation of *fac*-[(dppe)(CO)₃Cr=C(OMe)(Me)] in THF,⁽⁶⁾⁹ under nitrogen, with 1 equiv. of 2.5 M *n*-BuLi at -78°C , followed after 30 min by addition of 1 equiv. of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and 1.1 equiv. of propylene oxide. The mixture was allowed to react for 2 h and then warmed to room temperature. After quenching with water and extracting with diethyl ether, the red-orange crude product was eluted on a flash column using 60:40 petroleum ether/benzene solvent. After evaporation at reduced pressure, the residue was crystal-

lized by slow diffusion of hexanes into a solution of crude **4** in a minimum of benzene to obtain red crystals in 66% yield.

X-ray quality single crystals of **1–4** were obtained by slow diffusion of the top layer of approximately 2 mL of methanol into the bottom layer of 80–120 mg of the compound dissolved in a minimum of d^5 -pyridine in an NMR tube.⁽⁷⁾ The NMR tube was placed in a freezer at -10°C and allowed to crystallize over a period of several weeks.

NMR spectra. The ^1H NMR spectra of compounds **1–4** were obtained at 300.075 MHz on a Varian Gemini 300 spectrometer, in C_6D_6 , at room temperature, and referenced to residual C_6H_6 at 7.15 ppm. **1:** δ 7.67 (m, 4H), 7.50 (m, 4H), 6.87–7.02 (overlapping mults, 12H), 2.56 (s, 3H), 2.38–2.52 (overlapping mults, 6H), -0.14 (t, $J = 6.9$ Hz, 3H). **2:** δ 7.70 (m, 4H), 7.60 (m, 4H), 6.90–7.15 (overlapping mults, 15H), 6.56 (d, $J = 7.3$ Hz, 2H), 2.65–2.74 (m, 2H), 2.23–2.41 (m, 2H), 2.33 (s, 3H). **3:** δ 7.67 (m, 4H), 7.50 (m, 4H), 6.86–7.09 (overlapping mults, 12H), 2.6–2.8 (br s, 3H), 2.40–2.57 (m, 2H), 2.13–2.32 (m, 2H), 1.84 (s, 3H). **4:** δ 7.81 (m, 2H), 7.61 (m, 4H), 7.42 (m, 2H), 6.84–7.04 (overlapping mults, 12H), 3.79 (ddd, $J = 11.2, 8.3, 2.9$ Hz, 1H), 2.67–2.96 (overlapping mults, 2H), 2.40–2.54 (m, 2H), 2.00–2.14 (m, 2H), 0.78 (m, 1H), 0.24 (m, 1H), 0.04 (d, $J = 6.2$ Hz, 3H).

Crystallography. Single crystals were selected from each NMR tube by viewing them under a stereomicroscope equipped with crossed polarizers. Single crystals of appropriate size were mounted to the tip of a 0.1-mm glass capillary with petroleum jelly. Data were collected from single crystals of each sample at -30°C on a SMART[©] 1000 CCD detector system using graphite-monochromated Mo $K\alpha$ radiation. An entire hemisphere of data was collected in multi-run mode with ω as the rotation axis. Detector-to-sample distance was 5.25 cm, and the detector 2θ angle was -28° . Rotation width was 0.3° , frame

⁽³⁾The detailed syntheses and characterizations of compounds **1–4** have been published (see Ref. 7).

⁽⁴⁾A similar preparation of compound **1** has been reported (see Ref. 6).

⁽⁵⁾Pentacarbonyl alkoxy carbenes $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})(\text{Me})$, $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Ph})$, $(\text{CO})_5\text{W}=\text{C}(\text{OMe})(\text{Me})$, and $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Me})$ are known compounds.

⁽⁶⁾The compound *fac*-(dppe)(CO)₃Cr=C(OMe)(Me) was prepared according to the procedure for **1** and **2** from the known pentacarbonyl Fischer carbene $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Me})$.

⁽⁷⁾Deuterated solvent was used as the dissolved samples were first subjected to NMR analysis. Presumably, nondeuterated pyridine could be used in its place.

size was 512×512 pixels, number of frames was 1868, data collection time per frame was 60 s, and the total time for data collection was ~ 36 h per data set.

SMART v5.618© was used for data collection, indexing of reflections, and determination of lattice parameters.¹⁰ SAINT+ v6.02© was used for integration of reflection intensities.¹¹ Absorption corrections were applied using SADABS.¹² SHELXTL v6.10© was used for data reduction, space group determination, structure determination, structure refinement, graphics, and structure reporting.¹³ All X-ray crystallographic hardware, including analysis programs and diffraction unit, are copyrights of Bruker AXS, Inc.

Details of crystal parameters, data collections and refinement results are summarized for **1–4** in Table 1. Refined atomic coordinates and

equivalent isotropic displacement factors for **1–4** are given in Tables 2–5, respectively. Selected bond distances and bond angles for **1–4** are listed in Table 6.

Results and discussion

Overall structural features

Complexes **1–3** crystallize in the $P2_1/c$ space group while **4** crystallizes in $Pna2_1$, each with four molecules per unit cell. The ORTEP diagrams with atomic numbering schemes and thermal ellipsoids are depicted in Figs. 1–4.¹⁴

The coordination geometry of complexes **1–4** is pseudo-octahedral with the greatest distortions from 90° bond angles associated

Table 1. Summary of Crystallographic Data and Intensity Data Collection for **1, 2, 3, and 4**

Compound	1	2	3	4
CCDC deposit no.	195045	195046	195047	195048
Chemical formula	C33 H32 Cr O4 P2	C37 H32 Cr O4 P2	C32 H30 W O4 P2	C34 H32 Cr O4 P2
Formula weight	606.53	654.57	724.35	618.54
Temperature, K	243	243	243	243
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Unit cell dimensions				
<i>a</i> , Å	11.2243(11)	11.8102(9)	11.3458(6)	22.6509(14)
<i>b</i> , Å	18.5998(18)	18.3152(14)	18.5772(9)	9.8118(6)
<i>c</i> , Å	15.1260(15)	15.0262(12)	15.3883(8)	13.7507(8)
α , deg	90	90	90	90
β , deg	107.056(4)	93.753(3)	108.576(6)	90
γ , deg	90	90	90	90
Volume	3019.0(5)	3243.3(4)	3074.5(3)	3056.0(3)
<i>Z</i>	4	4	4	4
Density (calculated), g/cm ³	1.334	1.341	1.565	1.344
Absorption coefficient, mm ^{−1}	0.521	0.49	3.895	0.516
Diffractometer/scan	Bruker SMART/CCD	Bruker SMART/CCD	Bruker SMART/CCD	Bruker SMART/CCD
Scan	ω scan	ω scan	ω scan	ω scan
θ range for data collection, deg	1.78–28.17	1.73–28.21	1.78–28.14	1.80–28.32
Reflections measured	25135	27122	25628	26591
Independent observed reflections	6852	7392	6944	7158
Independent reflections [$I > 2\sigma(I)$]	4555	6291	4812	5459
<i>R</i> _{int}	0.0805	0.0289	0.0762	0.047
Data/restraints/parameters	6852/0/489	7392/0/398	6944/0/354	7158/1/499
Goodness-of-fit on <i>F</i> ²	1.028	1.03	1.1	0.900
Final <i>R</i> Indices [$I > 2\sigma(I)$]	<i>R</i> ₁ = 0.0489, <i>wR</i> ₂ = 0.1002	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0843	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.0962	<i>R</i> ₁ = 0.0278, <i>wR</i> ₂ = 0.0571
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.0902, <i>wR</i> ₂ = 0.1130	<i>R</i> ₁ = 0.0376, <i>wR</i> ₂ = 0.0887	<i>R</i> ₁ = 0.1051, <i>wR</i> ₂ = 0.1055	<i>R</i> ₁ = 0.0410, <i>wR</i> ₂ = 0.0585

Table 2. Refined Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for **1**

Atom	x	y	z	U_{eq}
C1	0.3572(3)	0.27424(16)	0.04674(19)	0.0402(7)
C2	0.2486(3)	0.15200(16)	−0.02352(19)	0.0434(7)
C3	0.4851(3)	0.15395(16)	0.04077(19)	0.0436(7)
C4	0.3481(2)	0.08033(15)	0.13223(17)	0.0365(6)
C5	0.3703(3)	0.01177(17)	0.0884(2)	0.0563(8)
C6	0.3003(3)	0.00178(17)	0.2499(2)	0.0555(8)
C7	0.2424(4)	0.01729(19)	0.3254(2)	0.0629(10)
C8	0.0716(2)	0.15393(15)	0.15502(18)	0.0350(6)
C9	−0.0016(3)	0.16682(18)	0.2126(2)	0.0521(8)
C10	−0.0992(3)	0.1224(2)	0.2124(3)	0.0672(10)
C11	−0.1250(3)	0.0633(2)	0.1553(2)	0.0605(9)
C12	−0.0538(3)	0.04970(19)	0.0977(2)	0.0583(9)
C13	0.0431(3)	0.09498(17)	0.09706(19)	0.0449(7)
C14	0.1135(3)	0.29500(15)	0.11058(18)	0.0365(6)
C15	0.1170(3)	0.35709(16)	0.1606(2)	0.0436(7)
C16	0.0440(3)	0.41585(18)	0.1225(3)	0.0564(9)
C17	−0.0339(3)	0.4128(2)	0.0347(3)	0.0652(10)
C18	−0.0393(4)	0.3510(2)	−0.0160(3)	0.0728(11)
C19	0.0336(3)	0.29315(19)	0.0206(2)	0.0600(9)
C20	0.2738(2)	0.23163(15)	0.27871(16)	0.0351(6)
C21	0.4013(2)	0.26537(15)	0.29347(18)	0.0379(6)
C22	0.6321(3)	0.26622(15)	0.24790(19)	0.0390(6)
C23	0.7008(3)	0.28949(17)	0.3354(2)	0.0511(8)
C24	0.8118(3)	0.32529(18)	0.3485(2)	0.0596(9)
C25	0.8574(3)	0.33833(18)	0.2757(3)	0.0615(9)
C26	0.7904(3)	0.31729(19)	0.1883(3)	0.0635(9)
C27	0.6776(3)	0.28115(17)	0.1745(2)	0.0490(8)
C28	0.5570(2)	0.13812(15)	0.31051(18)	0.0353(6)
C29	0.5472(3)	0.13087(18)	0.39917(19)	0.0486(8)
C30	0.5935(3)	0.0705(2)	0.4511(2)	0.0630(10)
C31	0.6501(3)	0.0176(2)	0.4173(3)	0.0653(10)
C32	0.6632(3)	0.02477(18)	0.3294(2)	0.0572(9)
C33	0.6172(3)	0.08430(16)	0.2766(2)	0.0437(7)
Cr1	0.35726(4)	0.17975(2)	0.08693(3)	0.03197(12)
O1	0.3549(2)	0.33258(12)	0.02008(17)	0.0668(7)
O2	0.1836(2)	0.13184(14)	−0.09421(14)	0.0673(7)
O3	0.5627(2)	0.13744(14)	0.00873(16)	0.0672(7)
O4	0.31622(17)	0.07105(10)	0.20998(12)	0.0392(4)
P1	0.20152(6)	0.21356(4)	0.15482(4)	0.03131(16)
P2	0.49115(6)	0.21253(4)	0.23284(4)	0.03264(17)

with the chelating dppe ligand, which is constrained to a five-member ring (average bite angle, $\text{P}(1)\text{—M—P}(2) = 82.51(3)^\circ$). In each complex, this ring adopts the most common twist (C_2 symmetry) conformation noted for dppe complexes,¹⁵ similar to that of a related tungsten nitrene complex, *fac*-(dppe)(CO)₃W = NNMe₂.¹⁶ The M—P(1) and M—P(2) bond distances in **1**, **2**, and **4** fall within a narrow range, from

Table 3. Refined Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for **2**

Atom	x	y	z	U_{eq}
C1	0.65687(13)	0.27575(9)	0.94374(10)	0.0374(3)
C2	0.81253(13)	0.17113(8)	0.96687(10)	0.0368(3)
C3	0.60878(13)	0.13705(8)	0.97395(10)	0.0391(3)
C4	0.71635(11)	0.09357(8)	0.82749(10)	0.0335(3)
C5	0.75133(13)	0.02361(8)	0.87254(10)	0.0377(3)
C6	0.7252(2)	0.02355(11)	0.68920(13)	0.0621(5)
C7	0.86514(16)	0.00759(10)	0.88523(15)	0.0600(5)
C8	0.90117(18)	−0.05554(12)	0.92863(17)	0.0728(6)
C9	0.8240(2)	−0.10326(11)	0.95912(14)	0.0660(6)
C10	0.71053(19)	−0.08806(11)	0.94741(15)	0.0649(5)
C11	0.67346(16)	−0.02459(10)	0.90410(13)	0.0535(4)
C12	0.92167(12)	0.20420(8)	0.74372(10)	0.0332(3)
C13	0.94380(15)	0.20183(10)	0.65443(11)	0.0468(4)
C14	1.04805(17)	0.17742(11)	0.62899(13)	0.0559(5)
C15	1.13008(15)	0.15434(10)	0.69137(13)	0.0525(4)
C16	1.10880(14)	0.15525(10)	0.77969(13)	0.0515(4)
C17	1.00542(13)	0.18036(9)	0.80581(11)	0.0436(4)
C18	0.84821(12)	0.33653(8)	0.80852(11)	0.0367(3)
C19	0.86548(19)	0.38724(10)	0.74313(13)	0.0583(5)
C20	0.9132(2)	0.45494(11)	0.76577(17)	0.0740(6)
C21	0.94407(18)	0.47141(10)	0.85170(17)	0.0656(6)
C22	0.92872(17)	0.42167(11)	0.91752(15)	0.0601(5)
C23	0.88097(15)	0.35425(9)	0.89581(12)	0.0481(4)
C24	0.69912(13)	0.25589(9)	0.68063(10)	0.0387(3)
C25	0.57934(13)	0.27479(9)	0.70458(10)	0.0404(3)
C26	0.40484(12)	0.25786(8)	0.82546(11)	0.0384(3)
C27	0.33047(15)	0.29345(10)	0.76477(13)	0.0515(4)
C28	0.23464(16)	0.32794(11)	0.79223(17)	0.0633(5)
C29	0.21199(17)	0.32685(11)	0.88060(17)	0.0660(6)
C30	0.28366(17)	0.29135(12)	0.94139(15)	0.0635(5)
C31	0.38021(15)	0.25679(10)	0.91426(12)	0.0502(4)
C32	0.46617(12)	0.13356(9)	0.72896(11)	0.0407(3)
C33	0.46160(16)	0.12559(12)	0.63752(13)	0.0589(5)
C34	0.4168(2)	0.06230(16)	0.59795(18)	0.0815(8)
C35	0.3763(2)	0.00782(14)	0.6491(2)	0.0898(9)
C36	0.38007(19)	0.01535(12)	0.7400(2)	0.0775(7)
C37	0.42451(15)	0.07776(10)	0.77965(15)	0.0545(4)
Cr1	0.687478(18)	0.186011(12)	0.890247(14)	0.02919(7)
O1	0.63769(12)	0.33019(7)	0.97784(9)	0.0567(3)
O2	0.88801(11)	0.16144(8)	1.01823(8)	0.0561(3)
O3	0.56689(12)	0.10707(8)	1.03064(9)	0.0607(3)
O4	0.71126(10)	0.09061(6)	0.73904(7)	0.0426(3)
P1	0.79186(3)	0.244765(19)	0.78276(2)	0.02995(9)
P2	0.53125(3)	0.21121(2)	0.78922(2)	0.03234(9)

2.3536(3) to 2.3618(5) Å, while, as expected, the tungsten complex **3** has longer bonds that average 2.507(2) Å. The former values can be compared to the Cr—P distance of 2.42 Å found in *cis*-(PPh₃)(CO)₄Cr=C(OMe)(Me),¹ while the latter average can be compared to the average

Table 4. Refined Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.3780(7)	0.2767(5)	0.5599(6)	0.051(2)
C2	0.2656(8)	0.1432(5)	0.4819(6)	0.051(2)
C3	0.5216(8)	0.1506(5)	0.5553(6)	0.054(2)
C4	0.3761(7)	0.0669(4)	0.6507(5)	0.047(2)
C5	0.4019(11)	−0.0001(5)	0.6067(7)	0.095(4)
C6	0.3449(11)	−0.0133(5)	0.7700(7)	0.097(4)
C7	0.0899(7)	0.1475(4)	0.6712(5)	0.0421(18)
C8	0.0151(9)	0.1600(5)	0.7240(7)	0.077(3)
C9	−0.0843(10)	0.1158(6)	0.7191(9)	0.097(4)
C10	−0.1084(9)	0.0569(6)	0.6627(7)	0.072(3)
C11	−0.0373(8)	0.0436(5)	0.6089(6)	0.066(3)
C12	0.0631(7)	0.0898(5)	0.6140(6)	0.058(2)
C13	0.1287(7)	0.2902(4)	0.6257(6)	0.0442(19)
C14	0.1235(8)	0.3502(4)	0.6768(7)	0.057(2)
C15	0.0520(9)	0.4093(5)	0.6382(9)	0.074(3)
C16	−0.0177(10)	0.4093(6)	0.5495(10)	0.088(4)
C17	−0.0141(12)	0.3500(7)	0.4969(9)	0.110(5)
C18	0.0602(10)	0.2909(6)	0.5344(7)	0.083(3)
C19	0.2942(7)	0.2271(4)	0.7946(5)	0.046(2)
C20	0.4193(7)	0.2647(4)	0.8099(5)	0.048(2)
C21	0.6574(6)	0.2674(4)	0.7742(5)	0.0395(18)
C22	0.7242(8)	0.2919(5)	0.8610(6)	0.058(2)
C23	0.8344(8)	0.3298(5)	0.8725(8)	0.071(3)
C24	0.8779(8)	0.3433(4)	0.8004(9)	0.077(3)
C25	0.8084(8)	0.3190(5)	0.7144(7)	0.069(3)
C26	0.6986(8)	0.2820(5)	0.7011(6)	0.058(2)
C27	0.5816(7)	0.1395(4)	0.8389(5)	0.0448(19)
C28	0.5670(8)	0.1358(6)	0.9249(6)	0.067(3)
C29	0.6097(11)	0.0779(8)	0.9806(9)	0.102(4)
C30	0.6664(10)	0.0215(7)	0.9530(9)	0.093(4)
C31	0.6842(9)	0.0236(6)	0.8676(10)	0.093(4)
C32	0.6401(8)	0.0824(5)	0.8092(7)	0.060(2)
O1	0.3704(7)	0.3368(3)	0.5370(5)	0.089(2)
O2	0.1994(6)	0.1238(4)	0.4112(4)	0.078(2)
O3	0.6023(6)	0.1367(4)	0.5288(5)	0.079(2)
O4	0.3474(5)	0.0571(3)	0.7264(4)	0.0557(15)
P1	0.21846(17)	0.20874(11)	0.67174(13)	0.0386(5)
P2	0.51696(18)	0.21160(11)	0.75772(13)	0.0390(5)
W1	0.38122(3)	0.174482(16)	0.60107(2)	0.03626(10)

W—P distance of 2.507(4) Å found in *fac*-(dppe)(CO)₃W = NNMe₂.¹⁶

Bonding and conformation of the carbene functional groups

The bonding in the carbene functional group of Fischer alkoxy carbenes is typically described in terms of the two resonance contributors **5a** and

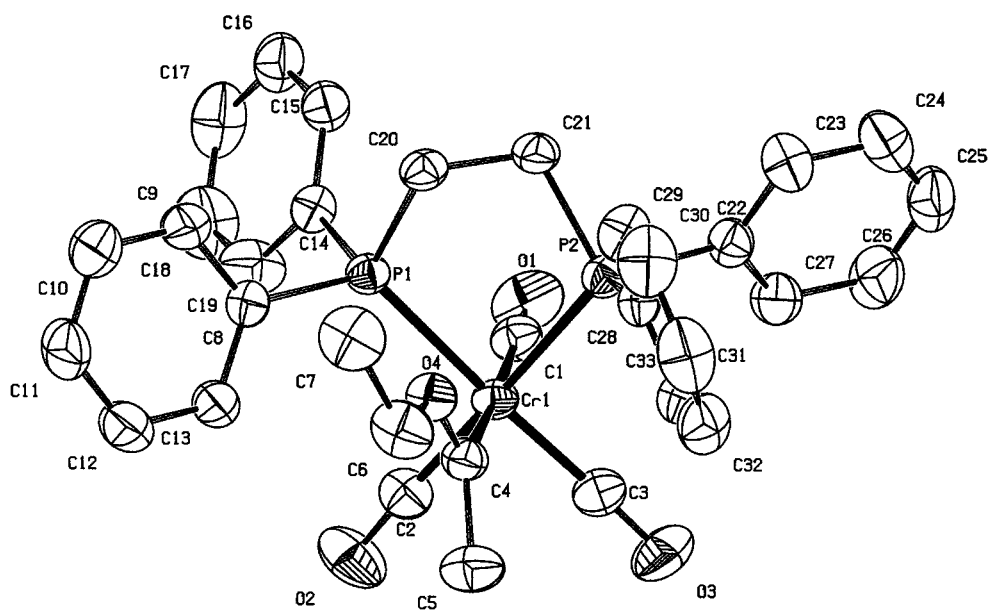
Table 5. Refined Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.02945(10)	0.6906(2)	0.26835(15)	0.0378(5)
C2	0.06594(9)	0.76459(19)	0.43993(16)	0.0382(5)
C3	0.14272(9)	0.65527(19)	0.32921(17)	0.0416(5)
C4	0.15498(9)	0.92155(18)	0.36403(14)	0.0342(5)
C5	0.19690(10)	0.9004(2)	0.44876(16)	0.0490(6)
C6	0.22309(11)	1.0392(2)	0.47058(17)	0.0572(7)
C7	0.22041(10)	1.1091(2)	0.37422(18)	0.0539(6)
C8	0.21151(13)	1.2576(2)	0.3695(2)	0.0774(9)
C9	0.04374(8)	1.14367(19)	0.37688(15)	0.0340(4)
C10	0.03321(10)	1.27891(19)	0.34916(16)	0.0457(6)
C11	0.03729(9)	1.3821(2)	0.41678(17)	0.0487(6)
C12	0.05074(9)	1.3550(2)	0.51210(18)	0.0470(6)
C13	0.06191(10)	1.2221(2)	0.54021(16)	0.0440(5)
C14	0.05843(9)	1.1179(2)	0.47265(15)	0.0375(5)
C15	−0.04493(8)	0.99121(19)	0.28216(15)	0.0346(4)
C16	−0.07921(10)	1.0766(2)	0.22417(16)	0.0452(6)
C17	−0.13967(11)	1.0691(2)	0.22584(18)	0.0542(6)
C18	−0.16801(10)	0.9773(2)	0.2853(2)	0.0581(7)
C19	−0.13507(10)	0.8911(2)	0.34248(17)	0.0510(6)
C20	−0.07400(9)	0.8977(2)	0.34069(15)	0.0414(5)
C21	0.06041(9)	1.0799(2)	0.17349(15)	0.0383(5)
C22	0.07346(9)	0.9669(2)	0.10003(14)	0.0383(5)
C23	0.11834(9)	0.6988(2)	0.06328(15)	0.0388(5)
C24	0.12241(10)	0.7271(2)	−0.03632(15)	0.0454(5)
C25	0.11830(10)	0.6242(3)	−0.10447(17)	0.0553(6)
C26	0.11082(11)	0.4906(3)	−0.07517(19)	0.0581(7)
C27	0.10767(11)	0.4611(2)	0.02278(19)	0.0611(7)
C28	0.11115(10)	0.5639(2)	0.09082(17)	0.0509(6)
C29	0.19714(9)	0.9003(2)	0.13471(14)	0.0356(5)
C30	0.20997(11)	1.0255(2)	0.09495(19)	0.0614(7)
C31	0.26741(13)	1.0711(3)	0.0886(2)	0.0788(9)
C32	0.31343(11)	0.9928(3)	0.1217(2)	0.0732(8)
C33	0.30163(10)	0.8687(3)	0.1611(2)	0.0653(7)
C34	0.24400(10)	0.8224(2)	0.16764(18)	0.0520(6)
Cr1	0.091294(12)	0.80000(3)	0.31505(2)	0.03107(7)
O1	−0.00901(7)	0.62093(16)	0.24376(11)	0.0542(4)
O2	0.05099(8)	0.73456(16)	0.51753(11)	0.0598(5)
O3	0.17615(7)	0.56822(16)	0.34103(13)	0.0662(5)
O4	0.16937(5)	1.04020(12)	0.32497(11)	0.0397(3)
P1	0.03656(2)	1.00180(5)	0.29020(4)	0.03176(11)
P2	0.12167(2)	0.83661(5)	0.15348(4)	0.03367(12)

5b in Fig. 5. The degree of double-bond character at the M—C_{carbene} and O—C_{carbene} bonding positions varies depending on the complex, but the partial double-bond character at the latter position can be sufficient to cause hindered rotation and the observation of *E* and *Z* isomers in solution.¹⁷ The isomers may be defined with respect to the disposition of the alkoxy group relative to the

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for **1**, **2**, **3**, and **4**

	1	2	3	4
Bond distances				
M(1)–C(1)	1.860(3)	1.8751(16)	1.998(9)	1.881(2)
M(1)–C(2)	1.829(3)	1.8326(15)	1.972(9)	1.842(2)
M(1)–C(3)	1.834(3)	1.8446(15)	1.986(8)	1.844(2)
M(1)–C(4)	1.986(3)	1.9784(15)	2.146(8)	1.991(2)
M(1)–P(1)	2.3578(8)	2.3552(4)	2.5054(19)	2.3618(5)
M(1)–P(2)	2.3569(8)	2.3569(4)	2.509(2)	2.3536(6)
C(1)–O(1)	1.155(3)	1.1504(19)	1.166(9)	1.155(2)
C(2)–O(2)	1.167(3)	1.1539(18)	1.164(9)	1.159(2)
C(3)–O(3)	1.156(3)	1.1520(19)	1.145(9)	1.158(2)
C(4)–O(4)	1.336(3)	1.3276(18)	1.319(8)	1.324(2)
C(4)–C(5)	1.490(4)	1.495(2)	1.491(12)	1.514(3)
Bond angles				
C(1)–M(1)–C(2)	91.83(13)	91.78(7)	92.6(3)	88.76(9)
C(2)–M(1)–C(3)	87.97(13)	85.45(7)	88.6(3)	87.46(10)
C(1)–M(1)–C(3)	92.75(13)	90.80(7)	92.0(3)	93.78(9)
C(1)–M(1)–C(4)	176.43(11)	176.85(6)	175.9(3)	178.09(8)
P(1)–M(1)–P(2)	82.74(3)	83.781(15)	79.91(6)	83.615(19)
C(2)–M(1)–P(2)	177.26(9)	176.84(5)	176.0(2)	177.64(6)
C(3)–M(1)–P(1)	176.66(9)	177.96(5)	174.8(2)	172.40(6)
O(4)–C(4)–C(5)	113.7(3)	114.29(12)	115.2(8)	106.17(17)
M(1)–C(4)–O(4)	118.61(18)	120.95(10)	119.0(6)	124.65(14)
M(1)–C(4)–C(5)	127.7(2)	124.68(10)	125.8(6)	129.18(15)

**Fig. 1.** Molecular structure of **1** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity.

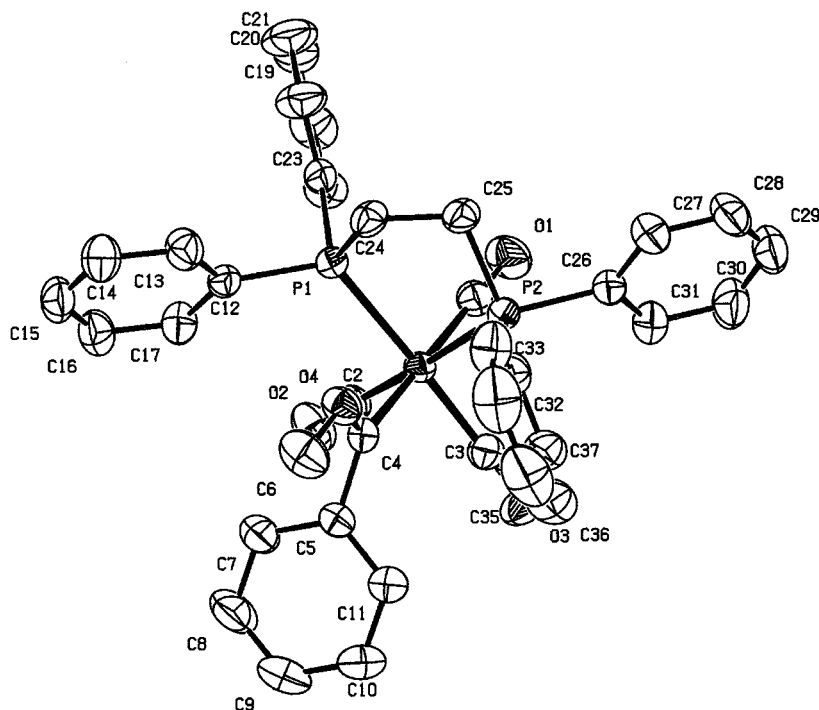


Fig. 2. Molecular structure of **2** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity.

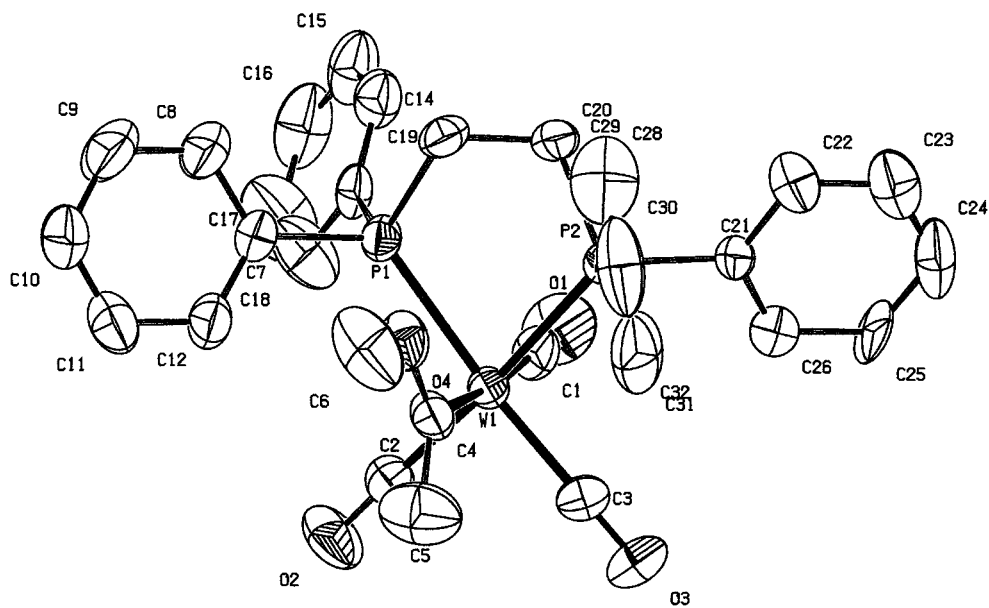


Fig. 3. Molecular structure of **3** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity.

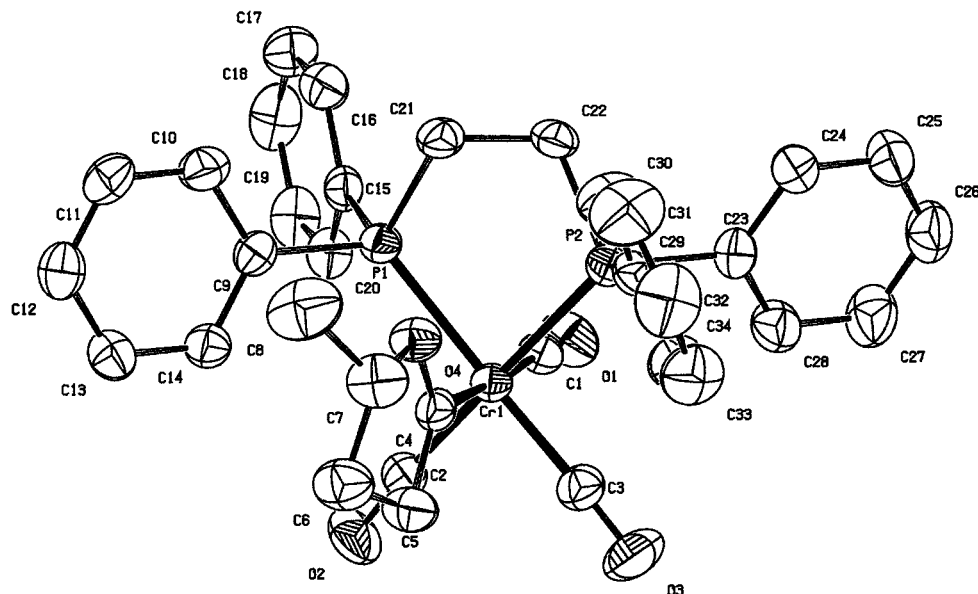


Fig. 4. Molecular structure of **4** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity.

metal along the O—C_{carbene} bond,¹⁸ as shown in the generalized structures for diphosphinated alkoxy carbene complexes in Fig. 6.

As expected, the metal atom, C(4), O(4), and C(5) in complexes **1–4**, respectively, are essentially coplanar due to the extended π -system over the former three atoms. This carbene plane approximately bisects the P(1)—M—P(2) bite angle, with angles to the plane containing P(1), M, and C(4) or P(2), M, and C(4) of 30–42°, typical values for Fischer carbenes.^{18,19} Structures **1–4** all adopt an *E* configuration, including, of course, **4** in which the ring structure of the carbene functionality requires this geometry. It is interesting to observe that, for **1–3**, the *E*

geometry is associated with the size of the angle between the metal and oxygen atoms attached to the carbene carbon (M—C(4)—O(4)), ranging from 118.61(18) to 120.95(10)°. ⁽⁸⁾ Literature reports on the X-ray structure analyses of pentacarbonyl Fischer alkoxy carbenes demonstrate that there is a clear trend in which *E* isomers adopt angles near 118°, ²⁰ while the *Z* isomers have angles near 132°, ²¹ apparently due to steric interactions between the alkoxy *R'* group and *cis* ligands at the metal.¹⁸ Although no general rule has been formulated for the prediction of *E* or *Z* geometries in pentacarbonyl or monophosphinated Fischer alkoxy carbenes, the reason for the *E* orientation in complexes **1–3** is clear: the *E* orientation minimizes steric interactions between the alkoxy group and the dppe ligand (vide infra).

The most striking feature of the structure of complexes **1–4** is the conformation of the carbene functionality relative to the diphosphine ligand. In every structure, the alkoxy moiety is oriented toward the diphosphine backbone, “sandwiched

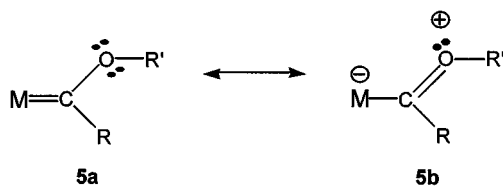


Fig. 5. Resonance structures **5a** and **5b**, describing bonding in the carbene fragment of Fischer alkoxy carbenes.

⁽⁸⁾Complex **4** necessarily has a somewhat larger M—C(4)—O(4) angle (124.65(14)°) as a consequence of the five-member ring.

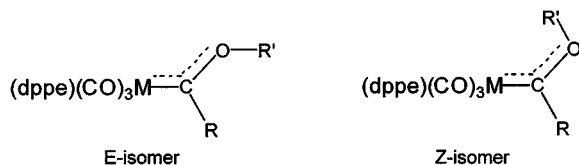


Fig. 6. Conformations of E- vs. Z-isomer in diphosphinated Fischer alkoxy carbenes.

between two diphosphine phenyl rings, one on each phosphorus atom.⁽⁹⁾ The alkyl or aryl carbene group, by contrast, is oriented away from the diphosphine backbone and lies outside of these phenyl rings. This includes the substituted 2-oxacyclopentylidene carbene functionality of **4** in which the oxygen heteroatom is directed toward the diphosphine backbone. The structures in Figs. 1–4 have been oriented to emphasize this conformation.

On the surface, this would appear to be a surprising result in that the solid-state structures place the ostensibly larger alkoxy moiety (e.g., $-OEt$ vs. $-Me$ in **1**)⁽¹⁰⁾ in the more sterically congested environment.⁽¹¹⁾²² It is clear, however, that the key to the conformational choice is a comparison of steric interactions that exist at O(4) compared to those that would exist at C(5) if the opposite conformation prevailed (i.e., 180° rotation about the $M-C(4)$ bond). For **1**, **3**, and **4**, the alkoxy oxygen, in which the attached alkyl group has an *E* orientation (i.e., directed away from the dppe backbone), has relatively little steric bulk in the direction of the dppe backbone or dppe phenyl rings. In the opposite conformation, the hydrogens on the tetrahedral C(5) atom would develop more significant steric interactions with the dppe backbone as well as the ipso and ortho carbons on the nearby dppe phenyl rings. The alternative

conformation for **2** presents even more significant steric repulsions when compared to the realized structure. Similar steric considerations are likely at work in the conformations of related dppe complexes involving carbene,²³ nitrene,¹⁶ and acylsilane functionalities.²⁴ Interestingly, analogous diphosphinated Fischer *amino* carbenes show just the opposite conformation of their carbene functionality, with the heteroatom amino functionality directed away from the diphosphine backbone and the alkyl carbene moiety “sandwiched” between two diphosphine phenyl rings.⁽¹²⁾²⁵

It is additionally possible that the observed conformation is stabilized by an electrostatic interaction between positive charge in the alkoxy group and π -electron density in the phenyl “sandwich.” The positive charge in the alkoxy functionality could result if resonance form **5b** makes a significant contribution to the electronic structure in these complexes. However, comparison of the relevant bond distances in chromium complexes **1**, **2**, and **4** with similar pentacarbonyl chromium carbenes suggest that this is unlikely. For example, the longest $Cr-C_{\text{carbene}}$ distance in these complexes ($1.991(2)$ Å for **4**) falls in the low end of the range of known chromium alkoxy carbenes.^{18,19(13)} It is also significantly shorter than this distance in typical pentacarbonyl amino carbenes, which are known to have more significant π -donation from the amino substituent, and significantly shorter than the calculated $Cr-C(sp^2)$ single-bond distance of 2.21 Å.¹⁹ Thus, partial positive charge at the O(4) would not seem reasonable in these complexes. In fact, atomic charges calculated for the pentacarbonyl

⁽⁹⁾For discussion, the $-CH_2CH_2-$ and $-OCH(Me)-$ fragments of the 3-methyl-2-oxacyclopentylidene ligand in **4** are considered to be the alkyl and alkoxy carbene substituents, respectively.

⁽¹⁰⁾The comparison of the sterics for **2** is less clear in that the larger, but planar, phenyl group is being compared to the smaller, but nonplanar, methoxy group.

⁽¹¹⁾¹H NMR results indicate that **1–4** adopt the same conformation in solution.

⁽¹²⁾The crystal structures of three new diphosphinated chromium Fischer amino carbenes with the compositions $fac-[(diphos)(CO)_3Cr=C(OR')(R)]$ ($R = Me$, $NR'_2 = \text{pyrrolidino}$, $diphos = dppe$; $R = Me$, $NR'_2 = \text{pyrrolidino}$, $diphos = dppp$; $R = Me$, $R' = Me$, $diphos = dppe$) have been determined in our laboratories. The detailed structures of these compounds will be published presently. However, a preliminary report of the structures of these compounds and compounds **1–4** has been published (See Ref. 25).

⁽¹³⁾The $C(4)-O(4)$ distances in **1**, **2**, and **4** are very near to these values in alkoxy complexes that have somewhat longer $Cr-C_{\text{carbene}}$ distances. However, the $C-O$ bond distance is known to be a less reliable tool for comparison. (see Refs. 18 and 19).

alkoxy carbene $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Me})$ suggest a slight negative charge of -0.14 for the methoxy oxygen, although the methoxy carbon is slightly positive at 0.10 .²⁶⁽¹⁴⁾

Structural comparisons with analogs

It is particularly informative to compare complexes **1** and **2** to the solid-state structures of their direct pentacarbonyl analogs, $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})(\text{Me})$ and $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Ph})$, which have been characterized by neutron diffraction^{21a} and X-ray diffraction,²⁷ respectively. In both cases, the $\text{Cr}-\text{C}_{\text{carbene}}$ bond distance of the diphosphinated species is significantly shorter than the analog, by 0.067 \AA for **1** and $0.06(3) \text{ \AA}$ for **2**. The $\text{C}(4)-\text{O}(4)$ bond distance in **1** is 0.022 \AA longer than its analog, but this bond in **2** is identical, within experimental error, to its analog. Overall,⁽¹³⁾ these results suggest that there is less contribution to structures **1** and **2** from resonance form **5b**, possibly because of the lesser π -acidity of the phosphine moieties compared to carbonyl ligands. However, the steric impact of the dppe ligands likely also plays a role, as reflected in the fact that **1** and **2** adopt an *E* geometry while their pentacarbonyl analogs adopt the *Z* geometry. Separately, it is worth noting that the plane of the carbene phenyl substituent is essentially perpendicular to the carbene plane in both **2** and its analog.

The X-ray structure of the pentacarbonyl analog of **3** has not been reported.⁽¹⁵⁾²⁸ As expected, the metal–ligand bond distances are longer for the third-row transition metal tungsten com-

plex **3** than the chromium complexes **1**, **2** and **4**.⁽¹⁶⁾²⁹ In particular, the $\text{W}-\text{C}_{\text{carbene}}$ bond length is $0.161(10) \text{ \AA}$ longer than the average of this distance for complexes **1**, **2** and **4**.⁽¹⁷⁾ Complex **3** is, however, quite similar in overall geometry to the chromium complexes.

Although the X-ray structure of the pentacarbonyl analog of **4** has not been reported,⁽¹⁸⁾³⁰ a variety of related 2-oxacyclopentylidene structures have been determined.^{23,31} In **4**, the ring adopts an envelope conformation, in which $\text{C}(6)$ is out of the plane, with $\text{C}(4)-\text{O}(4)-\text{C}(7)-\text{C}(6)$ and $\text{O}(4)-\text{C}(4)-\text{C}(5)-\text{C}(6)$ torsion angles that average $18.8(2)^\circ$. This is akin to the ring geometry adopted by pentacarbonyl $\{2', 2'\text{-dimethyl-3(S)-4'(R)-1', 3'\text{-dioxacyclopentyl)-2-oxacyclopentylidene}\}$ chromium(0).^{31a} The similarity between the ring conformations in these two 3-substituted 2-oxacyclopentylidene complexes suggests that dppe substitution does not play a major role in the ring conformation of **4**. Further, the envelope conformation of the 2-oxacyclopentylidene ligand has been observed in other related complexes.^{23,31b,c,e} As noted in comparing **1** and **2** to their pentacarbonyl analogs, the $\text{Cr}-\text{C}_{\text{carbene}}$ bond distance in **4** is somewhat shorter ($0.024(2) \text{ \AA}$) when compared to the above-mentioned pentacarbonyl analog.

Metal-to-carbonyl π -bonding

In metal carbonyls, the degree of metal-to-carbonyl π -bonding, and thus the $\text{M}-\text{C}_{\text{carbonyl}}$ bond length, is known to be particularly related to the nature of the ligand trans to the carbonyl.³² In addition, the $\text{M}-\text{C}$ bond lengths for carbonyl ligands trans to the carbene moiety have been correlated with the degree of π donation associated with the carbene ligand in pentacarbonyl

⁽¹⁴⁾Although the solid-state structure of $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Me})$ has not been determined, it might be reasonably be expected to have chromium–carbene carbon and carbene carbon–oxygen bond lengths that are similar to the known structure of $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})(\text{Me})$ (Ref. 21a). These bond lengths in the latter complex suggest, if anything, a greater contribution from resonance from **5b** than for the diphosphinated chromium alkoxy carbenes, **1**, **2**, or **4**.

⁽¹⁵⁾The pentacarbonyl and monophosphinated analogs of **3** have been synthesized (see Ref. 28).

⁽¹⁶⁾This is typical of tungsten alkoxy carbene complexes.

⁽¹⁷⁾This can be compared to $0.146(4) \text{ \AA}$ lengthening on going from chromium to tungsten for otherwise identical pentacarbonyl carbene complexes (Ref. 31a).

⁽¹⁸⁾The pentacarbonyl and monophosphinated analogs of **4** have been synthesized (see Ref. 30).

Fischer alkoxy and amino carbenes.¹⁹ In chromium complexes **1**, **2**, and **4**, the carbonyl ligands *trans* to the carbene moieties have an Cr—C bond length that ranges from 0.028(6) to 0.036(3) Å longer than the respective averages of the Cr—C bonds for the carbonyl ligands *trans* to phosphorus atoms. This may suggest that the extent of donation from the dppe phosphine moieties is greater than the carbene ligands.⁽¹⁹⁾³³ However, in *cis*-(PPh₃)(CO)₄Cr=C(OMe)(Me), the carbonyl *trans* to the carbene and the carbonyl *trans* to the phosphorus atom are reported to have equivalent Cr—C distances of 1.83 Å.¹ In all of these complexes, the steric impact of the dppe ligand may also affect the observed bond lengths. Interestingly, amino carbene ligands apparently show donating ability closer to that of the phosphine moieties in diphosphinated Fischer amino carbene complexes.⁽¹²⁾²⁵

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